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Thermodynamic properties of isomeric iso-butoxybenzoic acids: Experimental and theoretical study

Michał Jakubczyk[a], Andrzej Sporzyński[a], Vladimir N. Emel'yanenko[b], Mikhail A. Varfolomeev[b], Sergey P. Verevkin[b,c,*]

[a] Faculty of Chemistry, Warsaw University of Technology, 00-664 Warszawa, Poland
[b] Department of Physical Chemistry, Kazan Federal University, 420008 Kazan, Russia
[c] Department of Physical Chemistry and Department, Science and Technology of Life, Light and Matter, University of Rostock, D-18059 Rostock, Germany

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ABSTRACT

Standard (p° = 0.1 MPa) molar enthalpies of formation at the temperature T = 298.15 K of the 2-, 3-, and 4-iso-butoxybenzoic acids were measured using the combustion calorimetry. Standard molar enthalpies of vaporization and sublimation were derived from the vapor pressure temperature dependencies measured by the transpiration method. Molar enthalpies of the solid state phase transitions were measured by the DSC. Thermodynamic data on alkoxy substituted benzoic acids available in the literature were collected and combined with own experimental results. This data set on alkoxybenzoic acids was evaluated by using quantum-chemical and group-additivity methods.

1. Introduction

Alkoxybenzoic acids have become an object of recent increasing interest due to their new applications. They are used as flavoring substances and preservatives of fragrance in cosmetic formulations [1]. As some of them are natural products, they are good candidates for pharmaceutical co-crystals [1]. Several alkoxybenzoic acids and their derivatives reveal biological activity as inhibitors of phosphodiesterase [2]. The majority of the papers on alkoxybenzoic acids deals with *n*-alkoxy derivatives. It is due to their liquid crystal properties. Esters of these compounds with triethanolamine were found to be discotic mesogens [3]. It is noteworthy that these compounds easily form mixed supramolecular liquid crystals induced by hydrogen bonding which have a much wider mesophase range than their individual components [4,5]. For all the isomers of methoxybenzoic acid molecular and crystal structures have been determined by X-ray diffraction method [2,6]. The investigated compounds form dimeric molecules with a moderately strong intermolecular hydrogen bonds. Several polymorphs have been observed due to the flexibility of the molecule [1]. Thermochemistry of the methoxy substituted benzoic acids has been evaluated recently [7]. The molar enthalpy of formation and sublimation on benzoic acids with the *n*-alkoxy-substituents were also reported [8,9]. The lack of the data for branched alkoxy-substituted benzoic acids was the reason to investigate the iso-butoxy benzoic acids (see Fig. 1) in the present paper.

The new results together with the thermochemical data on alkoxybenzoic acid available in the literature (see Table 1) have been checked for internal consistency using the quantum chemical and the group-additivity methods.

2. Materials and methods

2.1. Materials

Samples of iso-butoxybenzoic acids were synthesized from the commercially available bromo-iso-butoxybenzenes according to a general procedure given on Fig. 2. Necessary details are given below for each isomer as follows.

* Corresponding author at: University of Rostock, Department of Physical Chemistry, Dr-Lorenz-Weg 1, 18059 Rostock, Germany. Tel.: +49 381 4986508; fax: +49 381 498 6502.
E-mail address: sergey.verevkin@uni-rostock.de (S.P. Verevkin).

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